Selective Vapor Deposition

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Types of Selective Depositions

Substrate composition-chemical selectivity

- **different reactivities with different substrate materials**
- **deactivation of reactive sites on certain materials**
- **different diffusion rates into different materials**

Substrate structure-physical selectivity

- **faster growth on tops of holes**
- **faster growth on bottoms of holes**

Types of Selective Depositions

Substrate composition

different reactivities with different substrate materials

Example: SiO_2 selectively deposited on TiO_2 but not on an organic dye

deactivation of reactive sites on certain materials

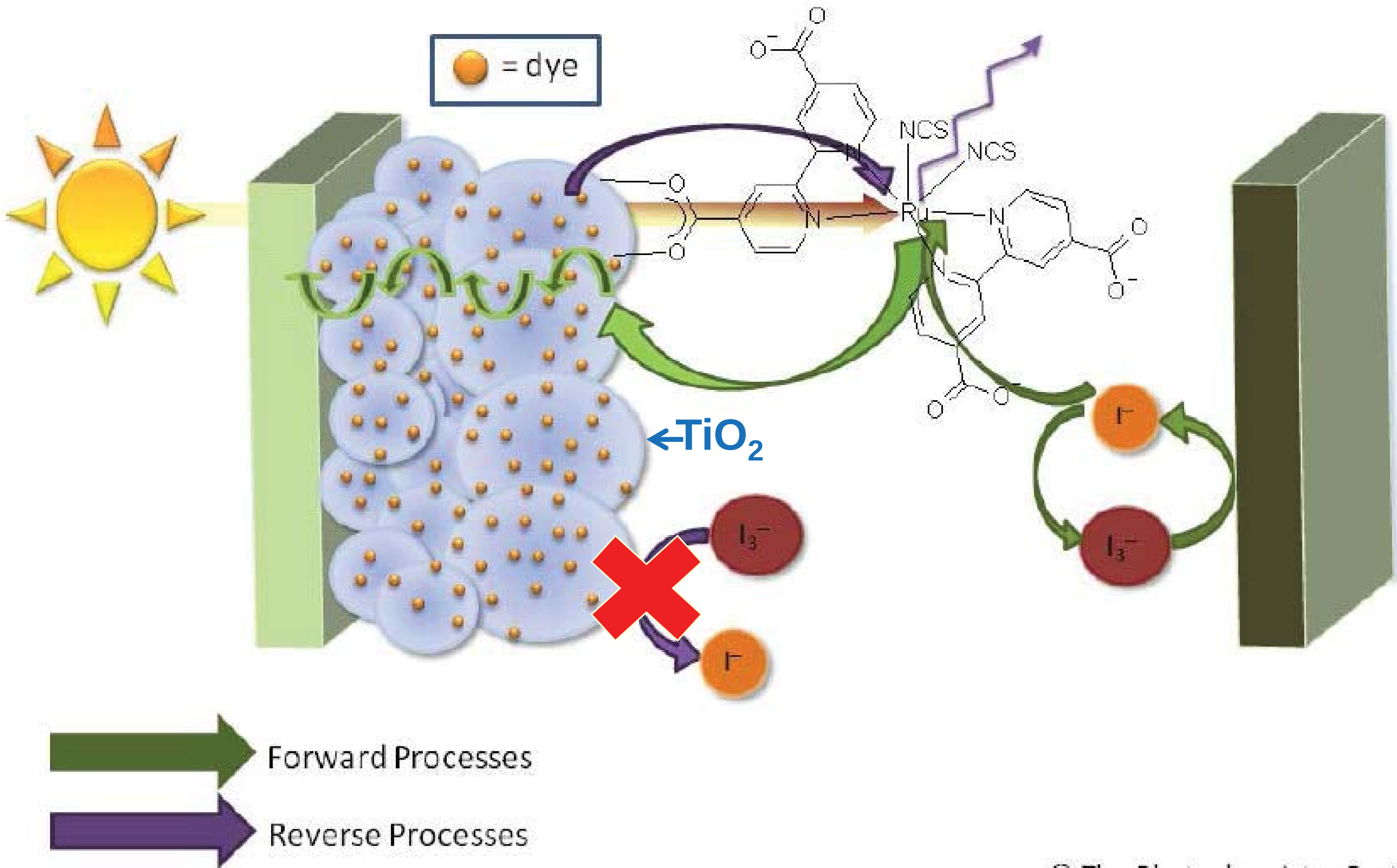
different diffusion rates into different materials

Substrate structure

faster growth on tops of holes

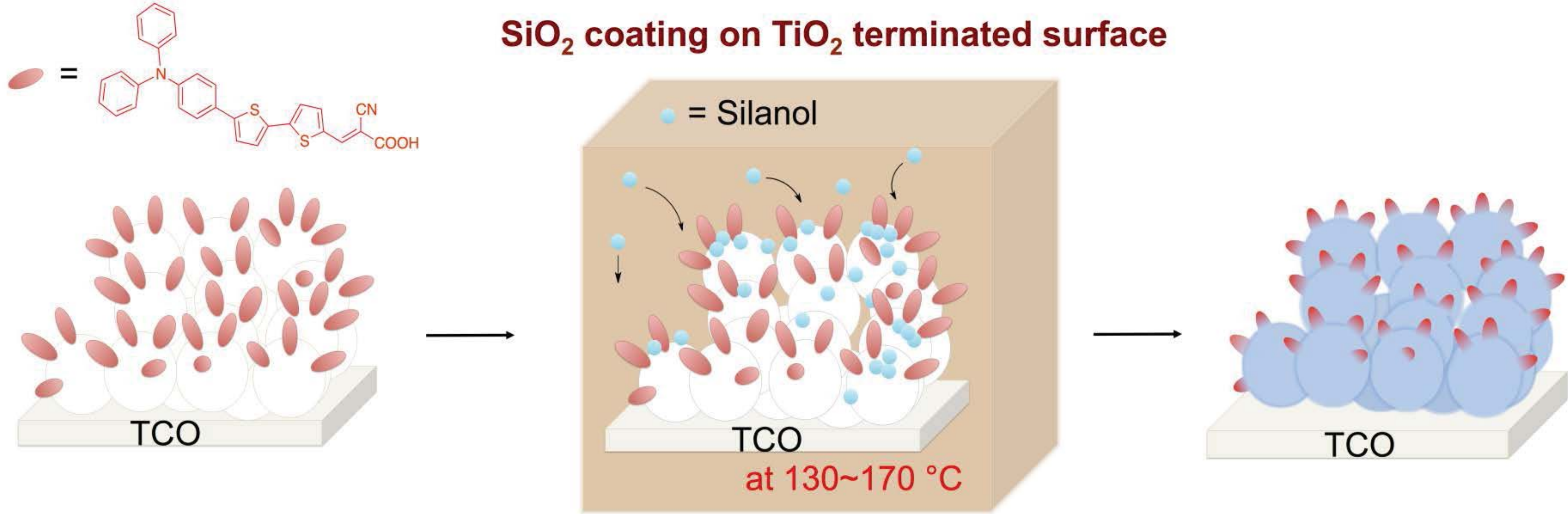
faster growth on bottoms of holes

Dye-Sensitized Solar Cells



ALD SiO_2 for Dye-Sensitized PV

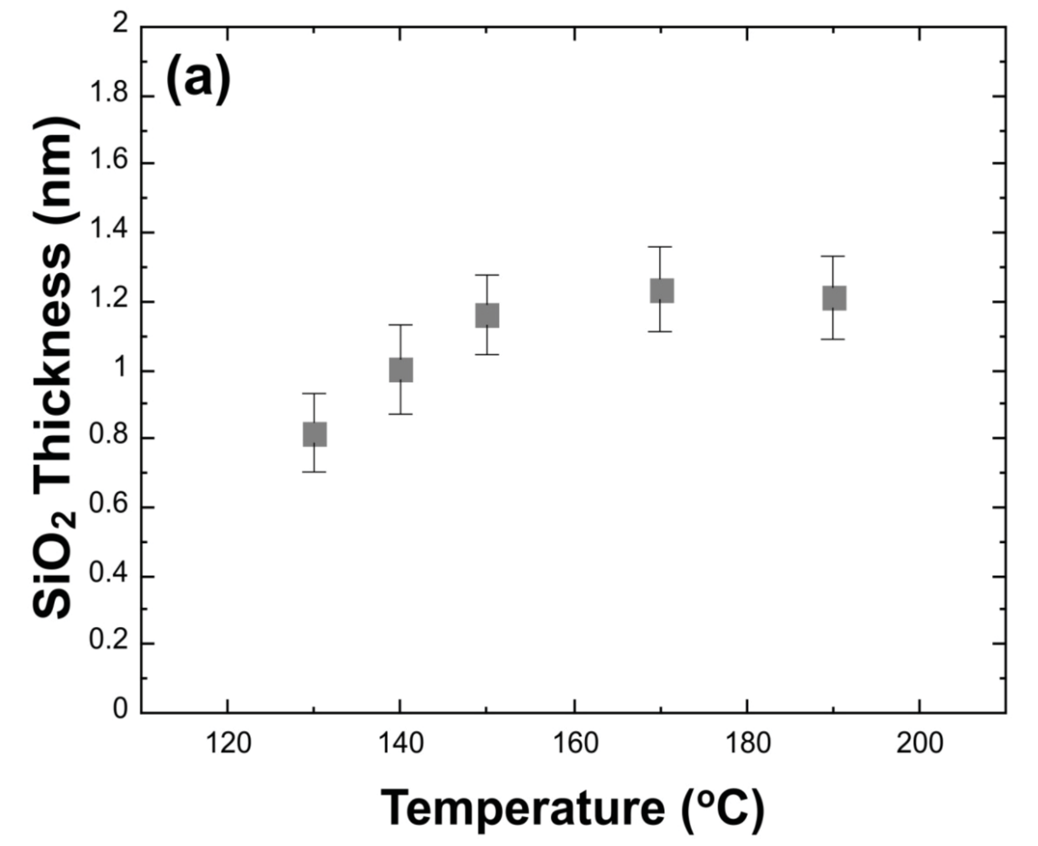
The solution: block leakage of electrons by ALD SiO_2 selectively on the areas of TiO_2 exposed to the electrolyte



½ ALD Cycle of SiO_2 on TiO_2

$((CH_3)_3CO)_3SiOH \Rightarrow SiO_2 + \text{volatile byproducts}$

Self-limited reaction catalyzed by TiO_2 surfaces

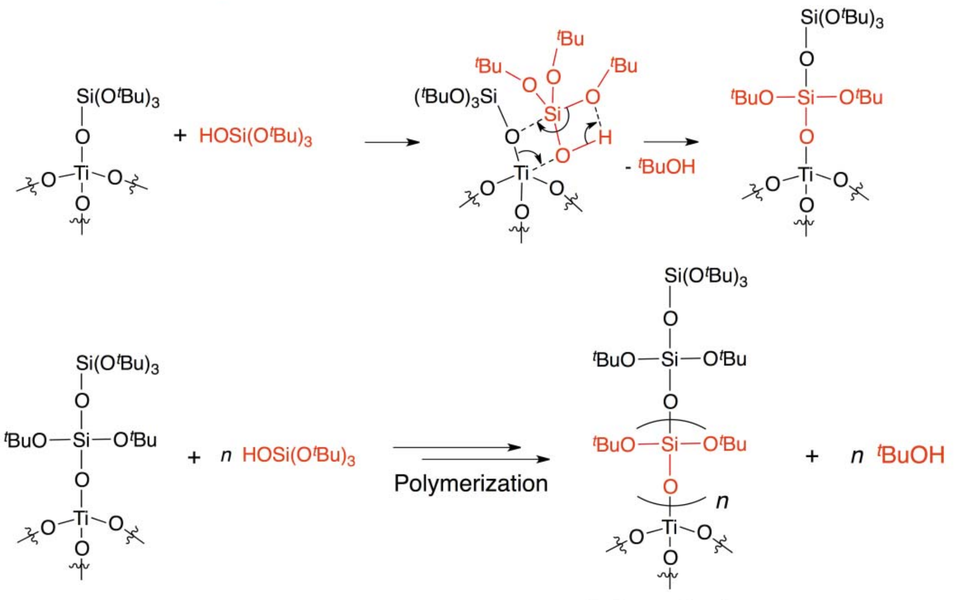


=> several monolayers of SiO_2!

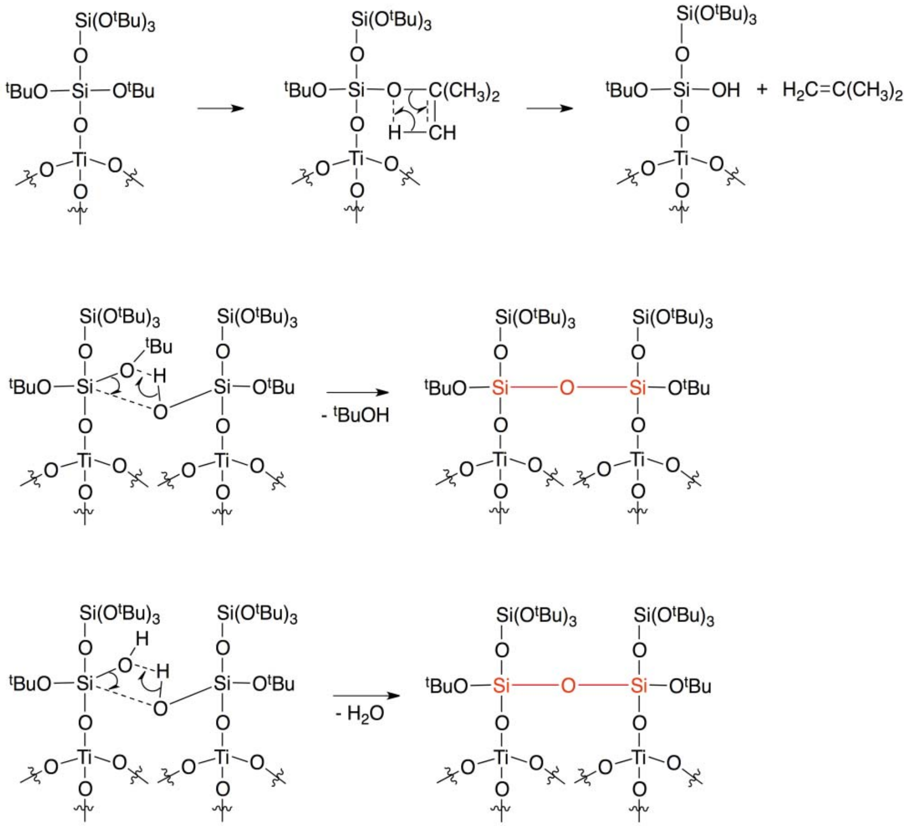
The reaction of silanol vapor with TiO_2 nanoparticles is complete within a few seconds.

ALD SiO_2 on TiO_2 Mechanism

A. Polymerization in vertical direction



B. Cross linking in horizontal direction

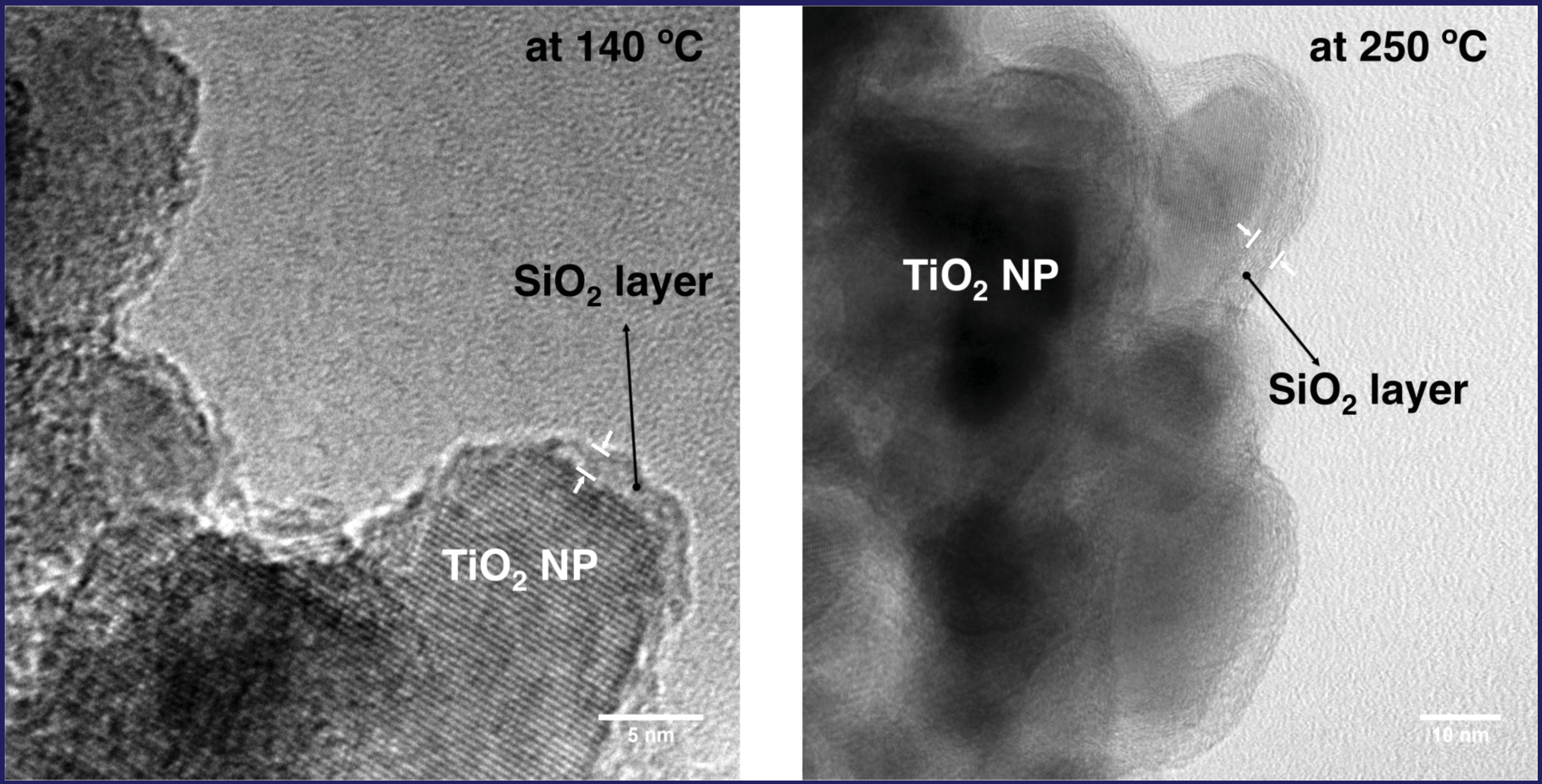


A similar catalytic mechanism was discovered for aluminum:

D. Hausmann, J. S. Becker, S. Wang and R. G. Gordon, *Science* 298, 402 (2002)

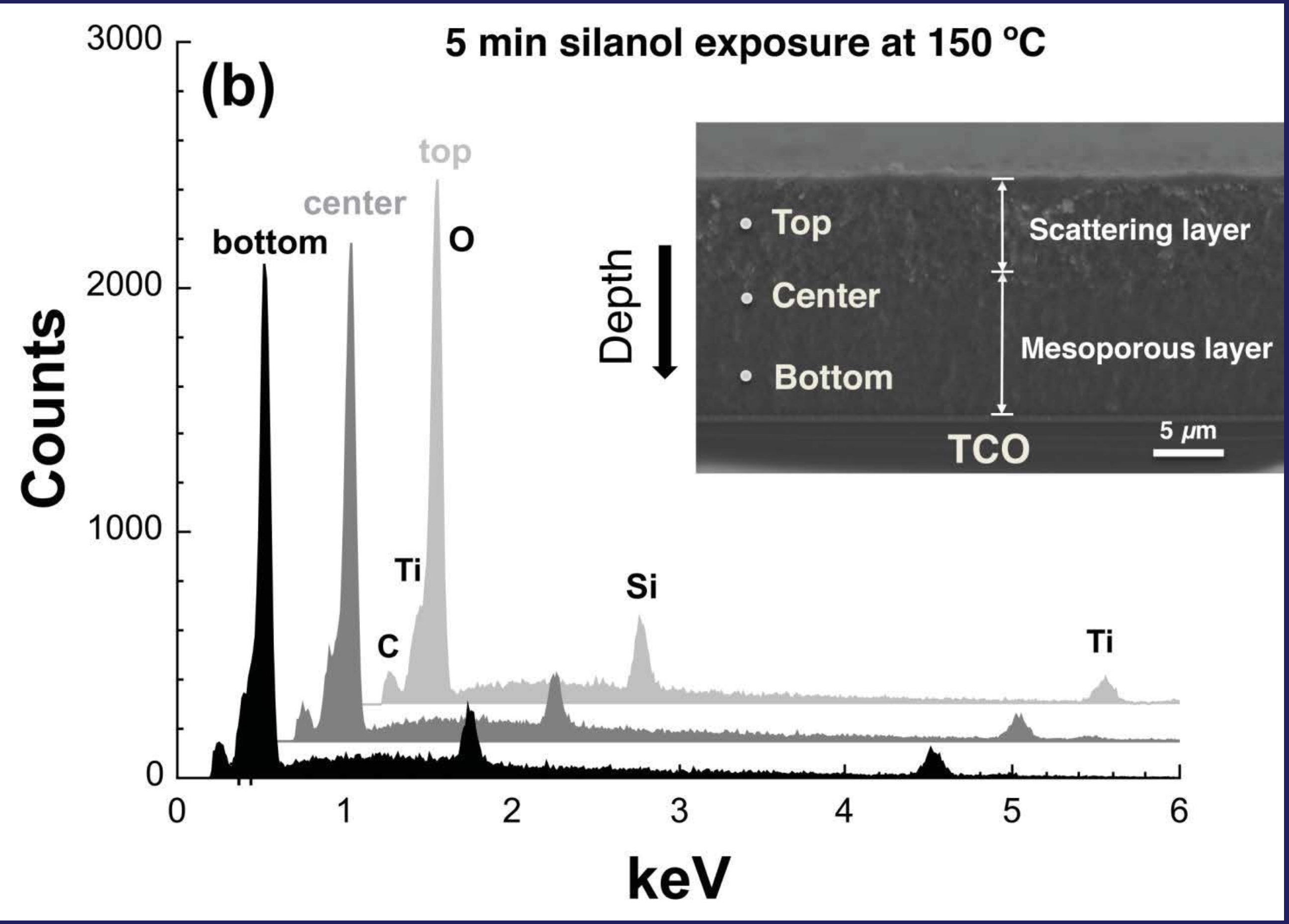
ALD of SiO_2 on TiO_2 Nanoparticles

=> Conformal SiO_2



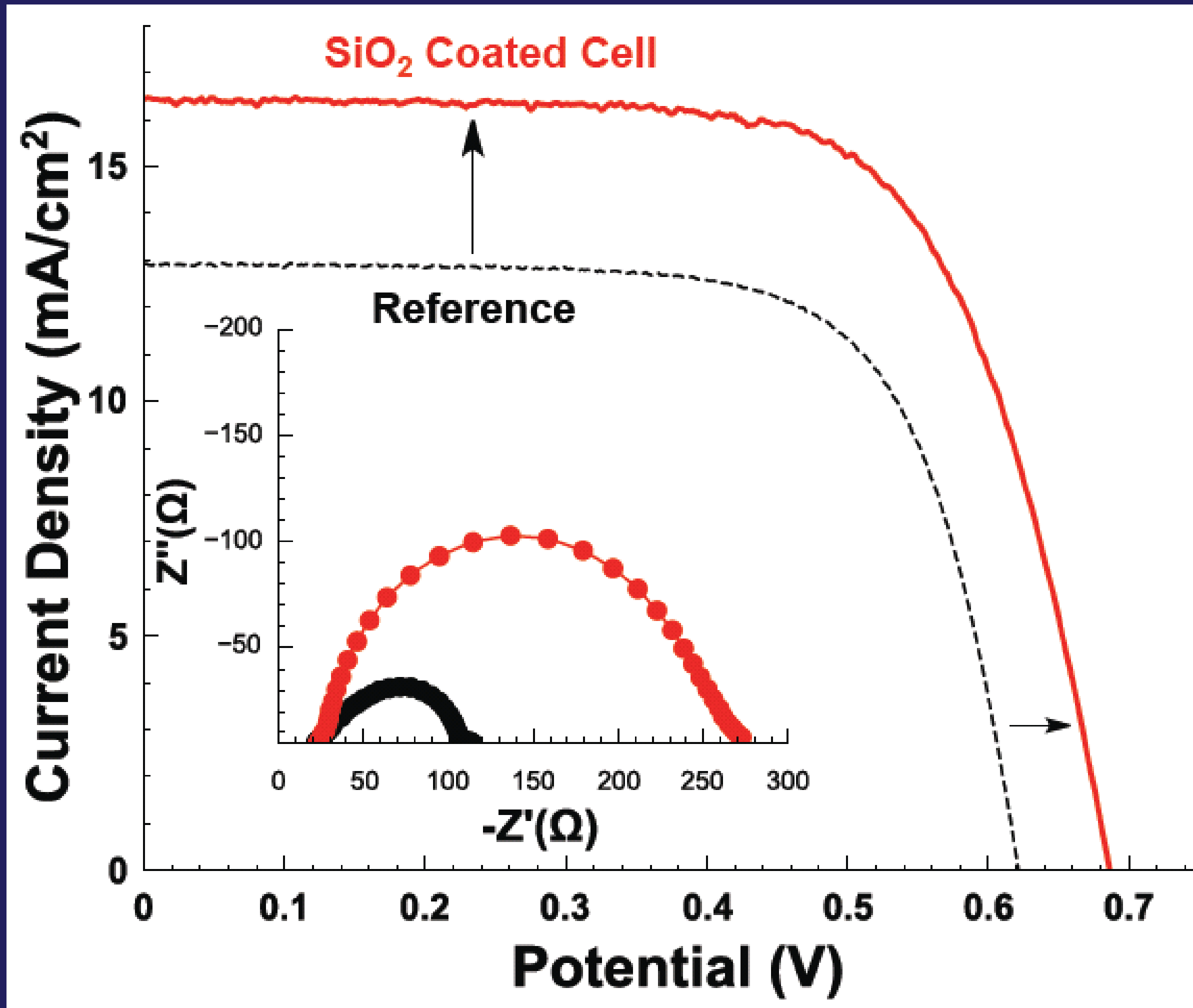
Uniformity of ALD SiO_2 on TiO_2

The thickness of the ALD SiO_2 is nearly constant through thousands of layers of TiO_2 nanoparticles.



ALD SiO_2 Improves PV Efficiency

36% relative increase in efficiency



Ho-Jin Son, Xinwei Wang, Chaiya Prasittichai, Nak Cheon Jeong, Titta Aaltonen, Roy G. Gordon, and Joseph T. Hupp, J. Amer. Chem. Soc. **134**, 9537 (2012)

Types of Selective Depositions

Substrate composition

different inherent reactivities with different materials

deactivation of reactive sites on some materials

Example: Surface passivation by self-assembled monolayers

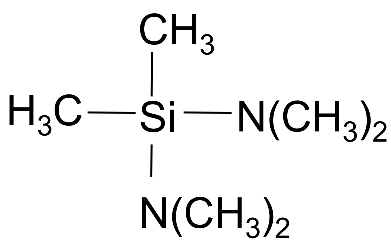
different diffusion rates into different materials

Substrate structure

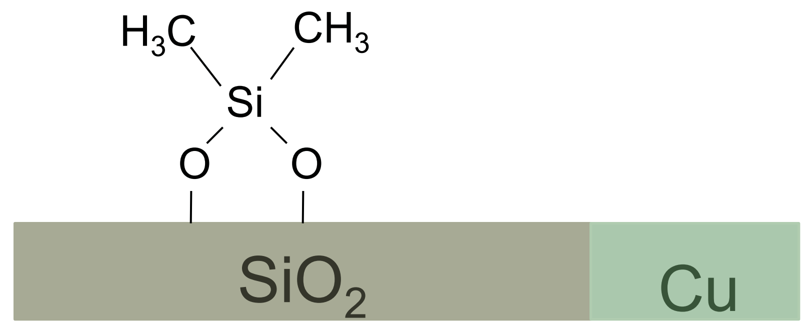
faster growth on tops of holes

faster growth on bottoms of holes

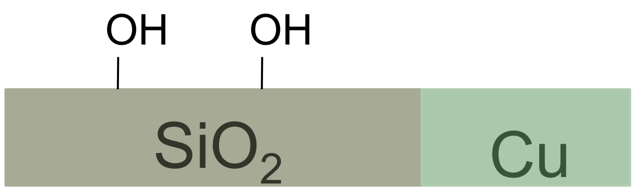
Selective Deactivation of Surface Hydroxyls

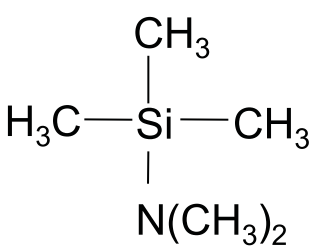


Bis(Dimethylamino)DimethylSilane (DADS)

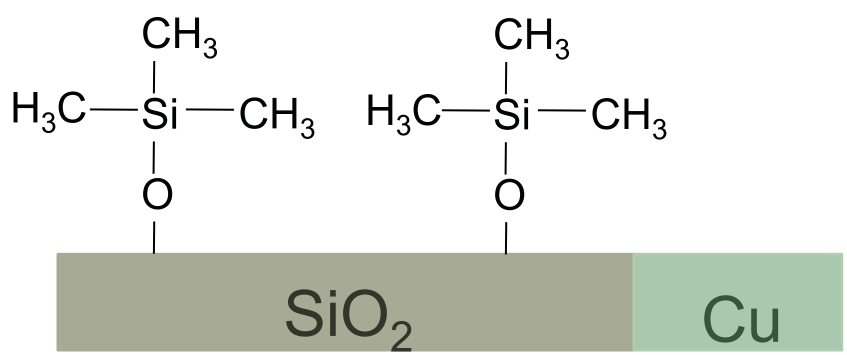


deactivates close pairs of OH groups





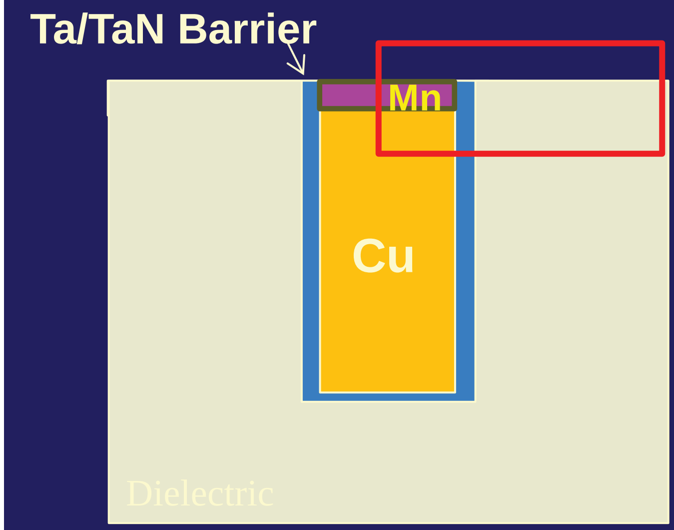
(N,N-Dimethylamino)TrimethylSilane (DATS)



deactivates isolated OH groups

Selective Deposition of CVD-Mn by Surface Passivation

Reduction by H_2 (250°C) → Surface Passivation by SAMs (90°C) → CVD-Mn Deposition (300°C)



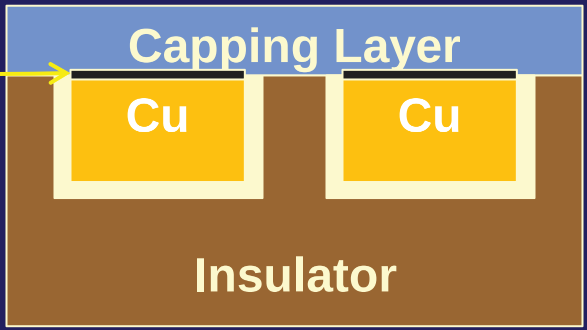
Mn only on Cu, not on insulator

EELS/EDX analyses

Son V. Nguyen, T. Vo, D. Priyadarshini, T. Haigh Jr., T. Nogami, S. Cohen, P. Flaitz, Y. Lin, H. Shobha, A. Grill, D. Canaperi and Roy Gordon, AVS ALD 2015 Conference

Increase lifetime before failure by electromigration

Self-aligned barrier/adhesion layer

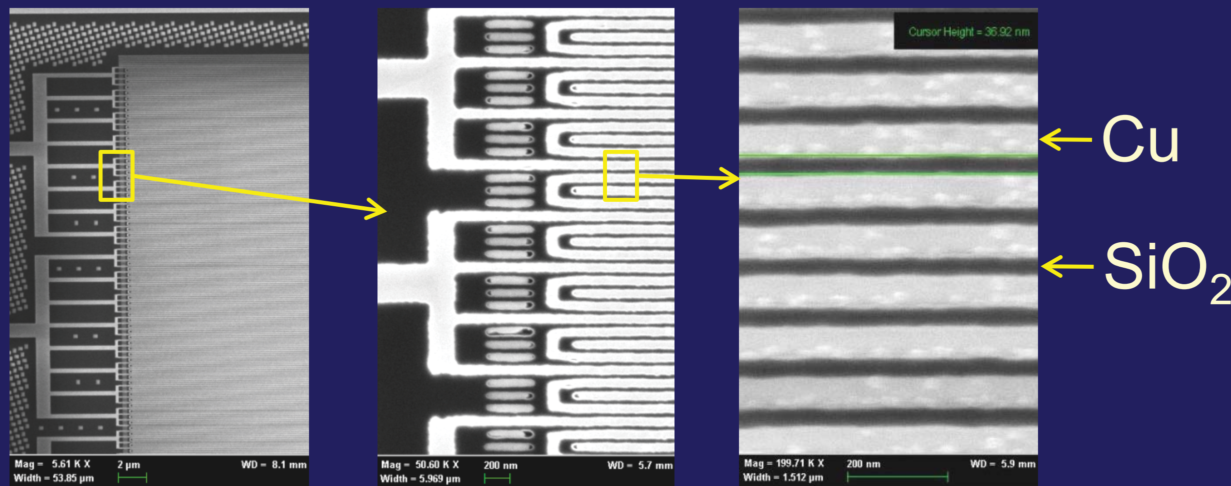


- Selectively deposit manganese on Cu wires to form a CuMn alloy
- Deposit capping insulator layer (Si_3N_4 or SiCN) on top
- Anneal to allow manganese to diffuse to the Cu/capping layer interface
- Manganese enhances adhesion at the interface and forms a self-aligned $MnSi_xO_yN_z$ diffusion barrier

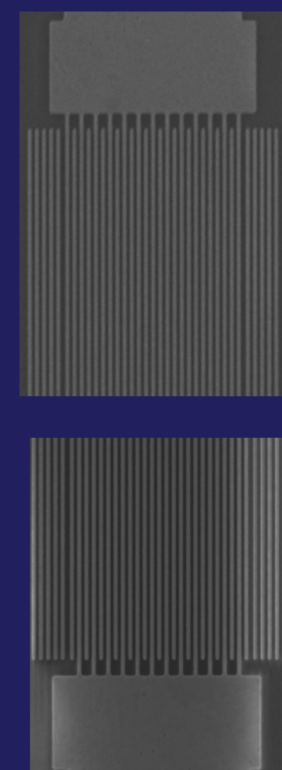
Y. Au, Y. Lin, H. Kim, E. Beh, Y. Liu and R. G. Gordon, "Selective Chemical Vapor Deposition of Manganese Self-Aligned Capping Layer for Cu Interconnections", *J. Electrochem. Soc.*, **157** (6) D341-D345 (2010)

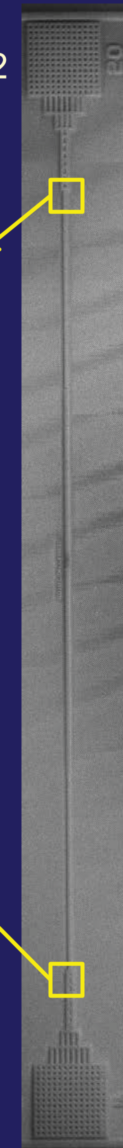
Selective Deposition of CVD-Mn by Surface Passivation

check leakage between Cu wires 10 m long separated by 40 nm of SiO_2



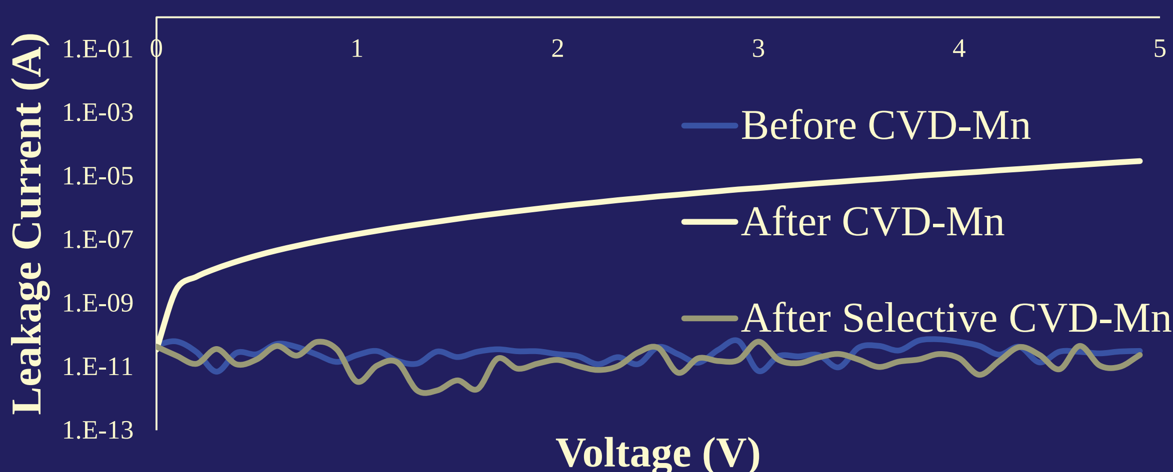
Substrate courtesy of IBM





Substrate courtesy of SELETE

Line-to-line Leakage Check



Selective deposition of CVD-Mn maintains the low leakage of the insulator

Types of Selective Depositions

Substrate composition

different reactivities with different substrate materials

deactivation of reactive sites on certain materials

different diffusion rates into different materials:

fast diffusion of Mn into Cu, but self-limited reaction with SiO_2

Substrate structure

faster growth on tops of holes

faster growth on bottoms of holes

Selectivity from bulk composition of substrates

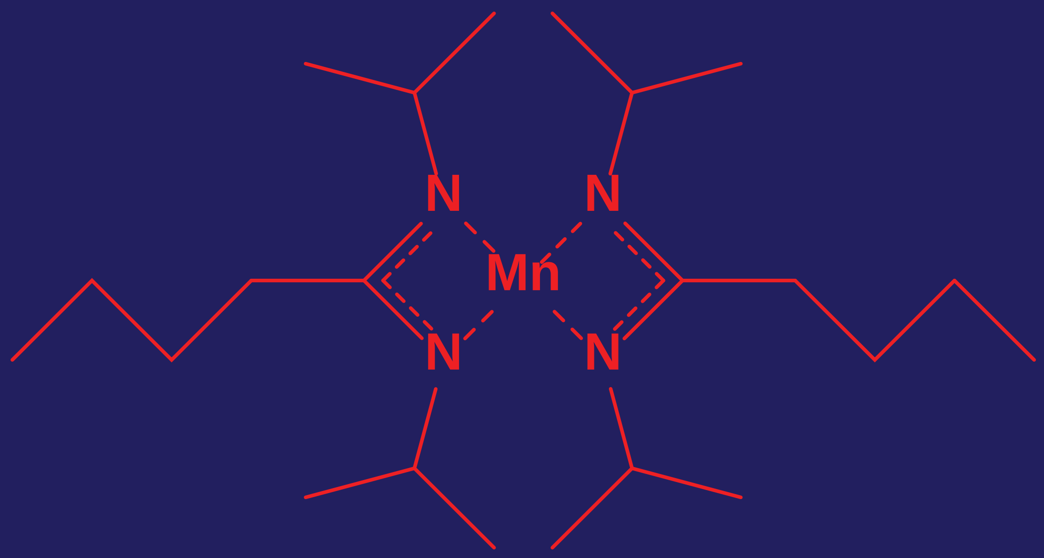
different diffusion rates of the deposit into different materials

MnNx deposition onto SiO_2 converts its surface into MnSixOy,
a barrier against diffusion of Cu, H_2O and O_2.

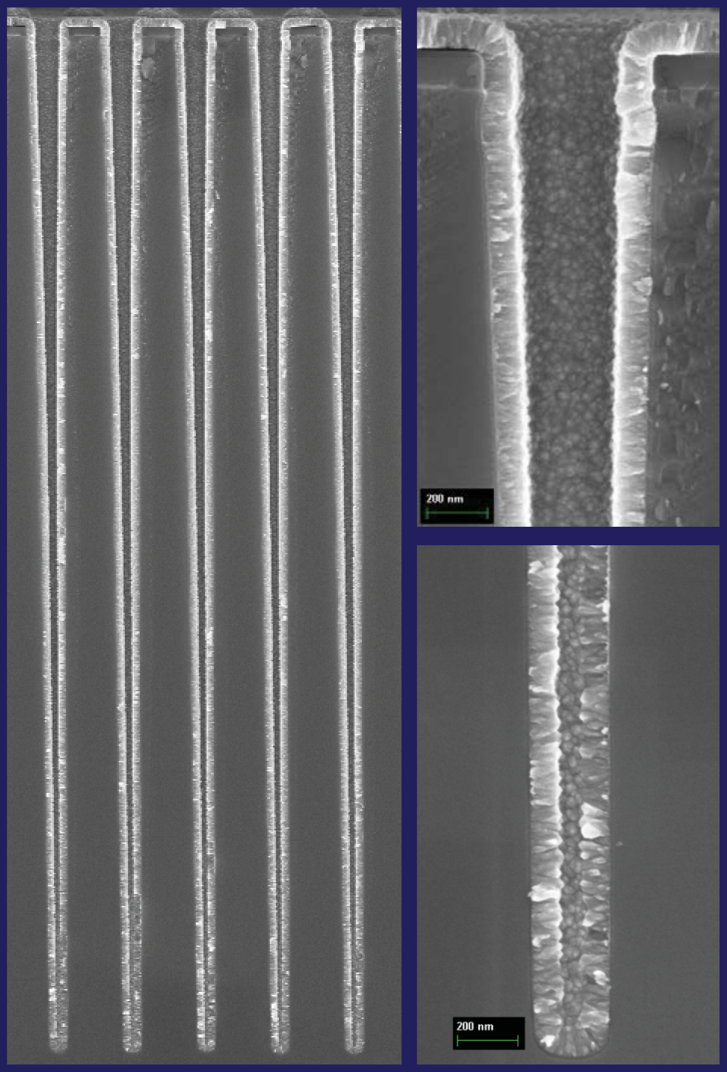
MnNx deposition onto Cu at via bottoms results in rapid diffusion
of both Mn and N away from the via bottoms to SiO_2 surfaces.

CVD-MnN_x Barrier/Adhesion/Iodine Adsorption Layer

Highly conformal MnN_x by CVD with NH_3 and manganese amidinate

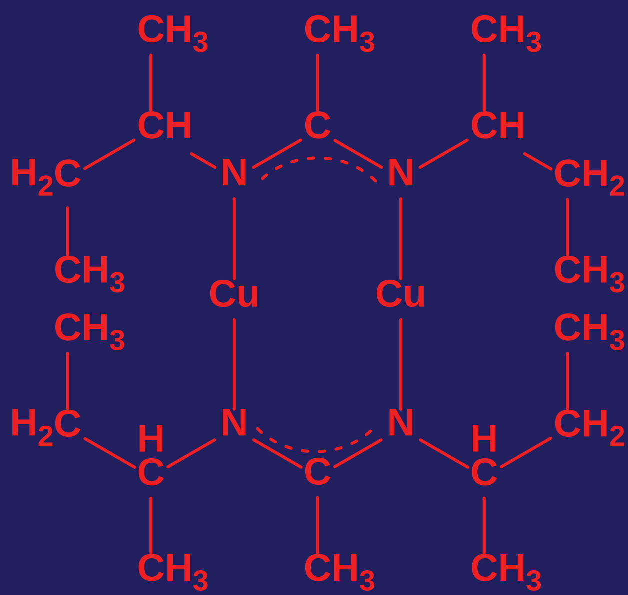


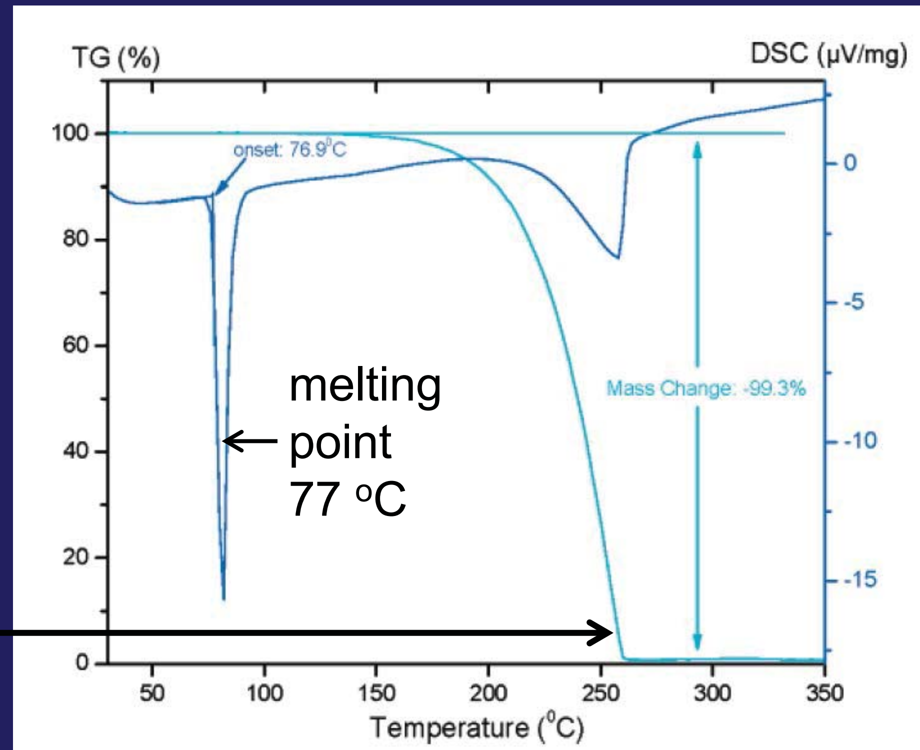
holes coated with CVD MnNx



Ethyl iodide dissociates on the MnN_x surface, selectively binds the iodine and releases byproduct ethyl groups.

Copper Amidinate Precursor

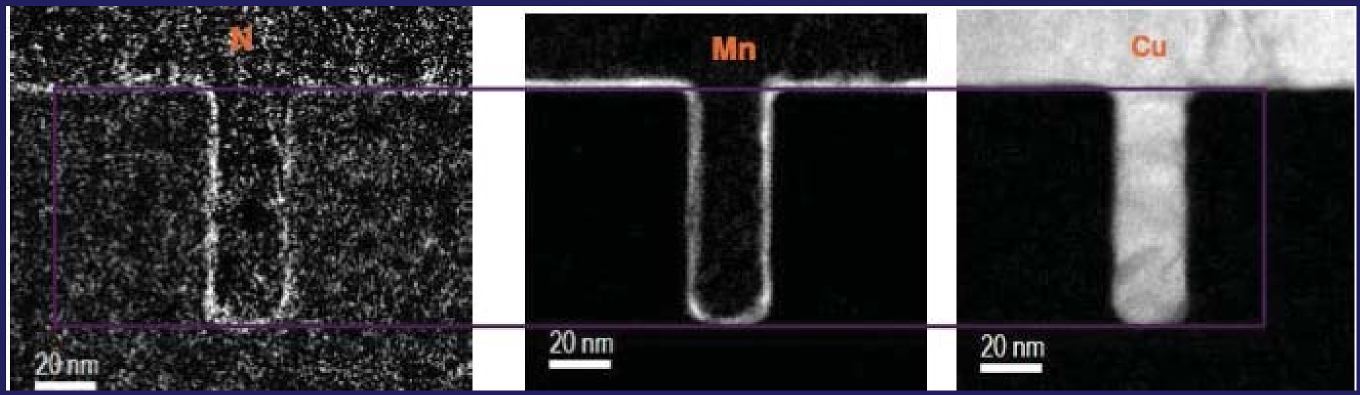




evaporation of copper amidinate with no residue

CVD with manganese and copper amidinates and H_2 deposits a copper-manganese alloy catalyzed by iodine

CVD Manganese Nitride, Iodine, Cu-Mn



TEM analysis shows Mn, N and Cu

void-free filling with Cu-Mn on MnN_x

Mn diffuses selectively from Cu-Mn to interfaces with SiO_2

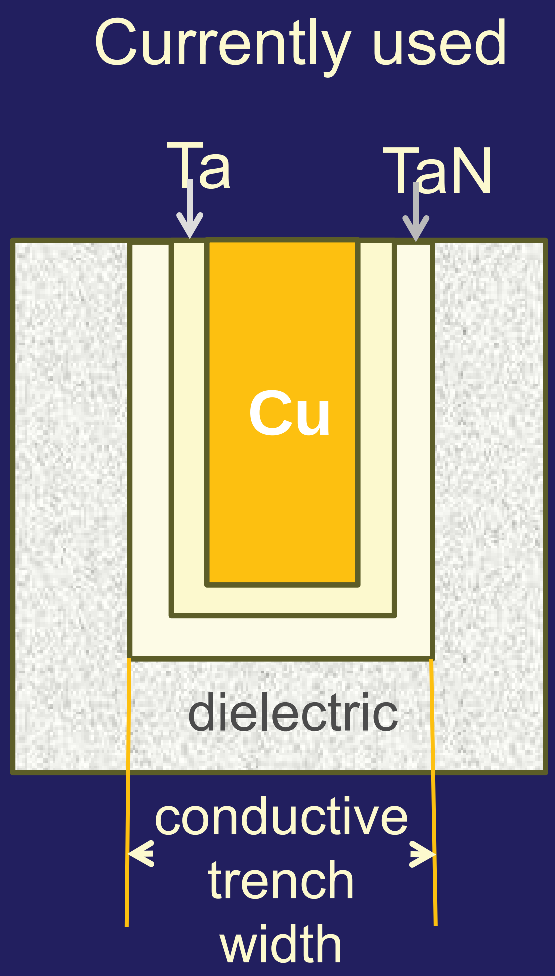
=> Strong adhesion between copper and SiO_2

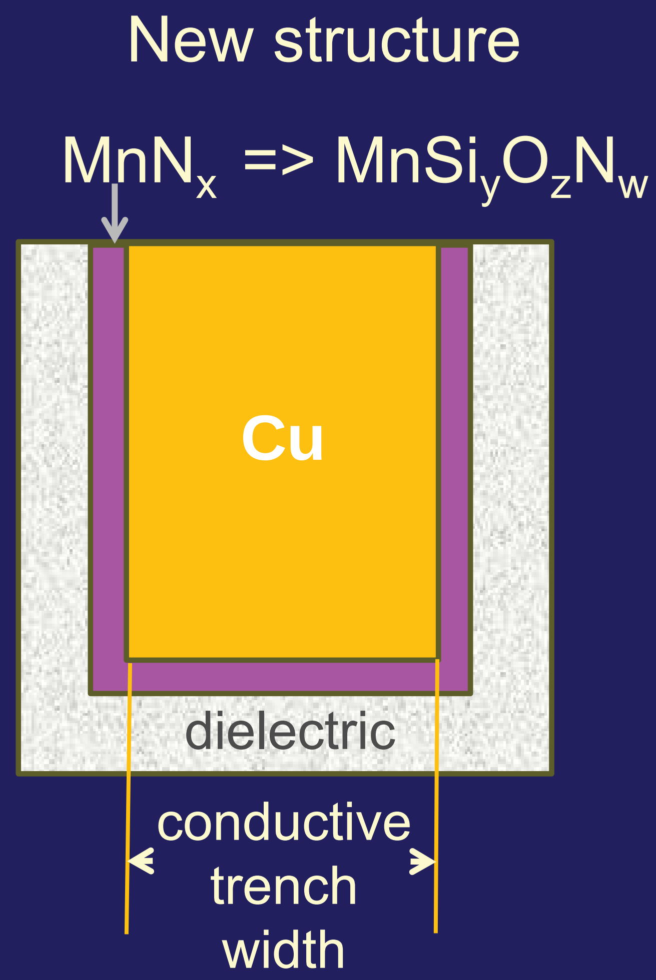
=> Forms $MnSi_xO_y$ diffusion barrier to Cu, H_2O and O_2

=> Conductivity and lifetime higher than conventional Cu/Ta

Reduced copper line resistances

More highly conductive Cu, less highly resistive Ta and TaN



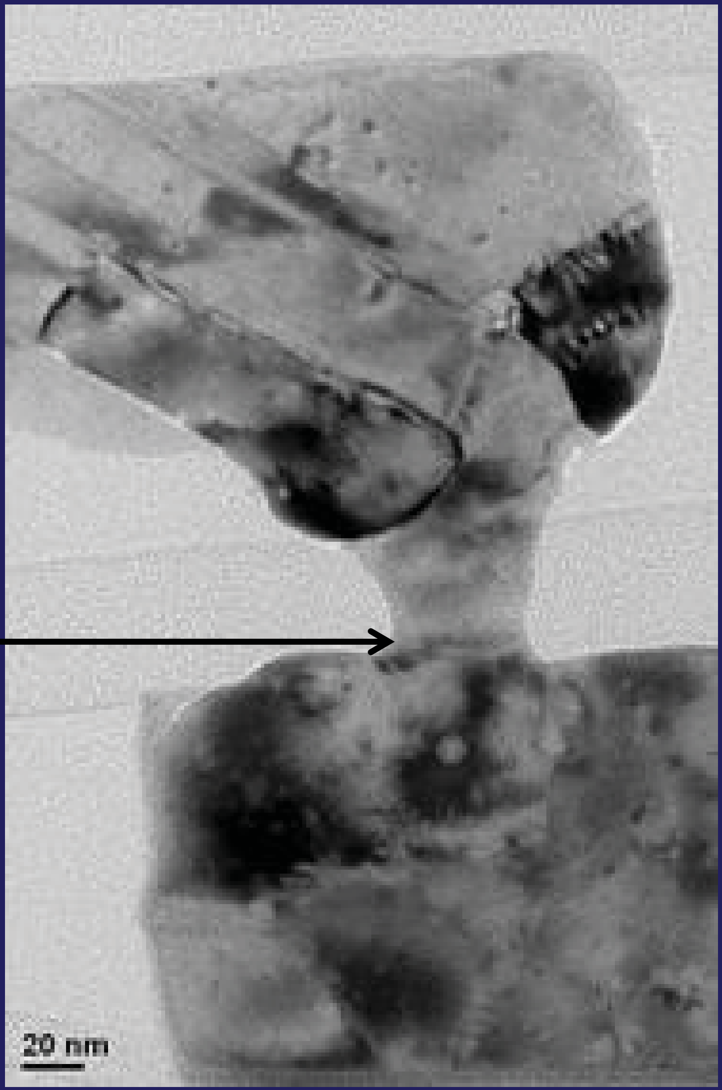


Cu Via Resistance Reduction by Mn Barrier

Mn selectively diffuses away from via bottoms to surfaces of insulators

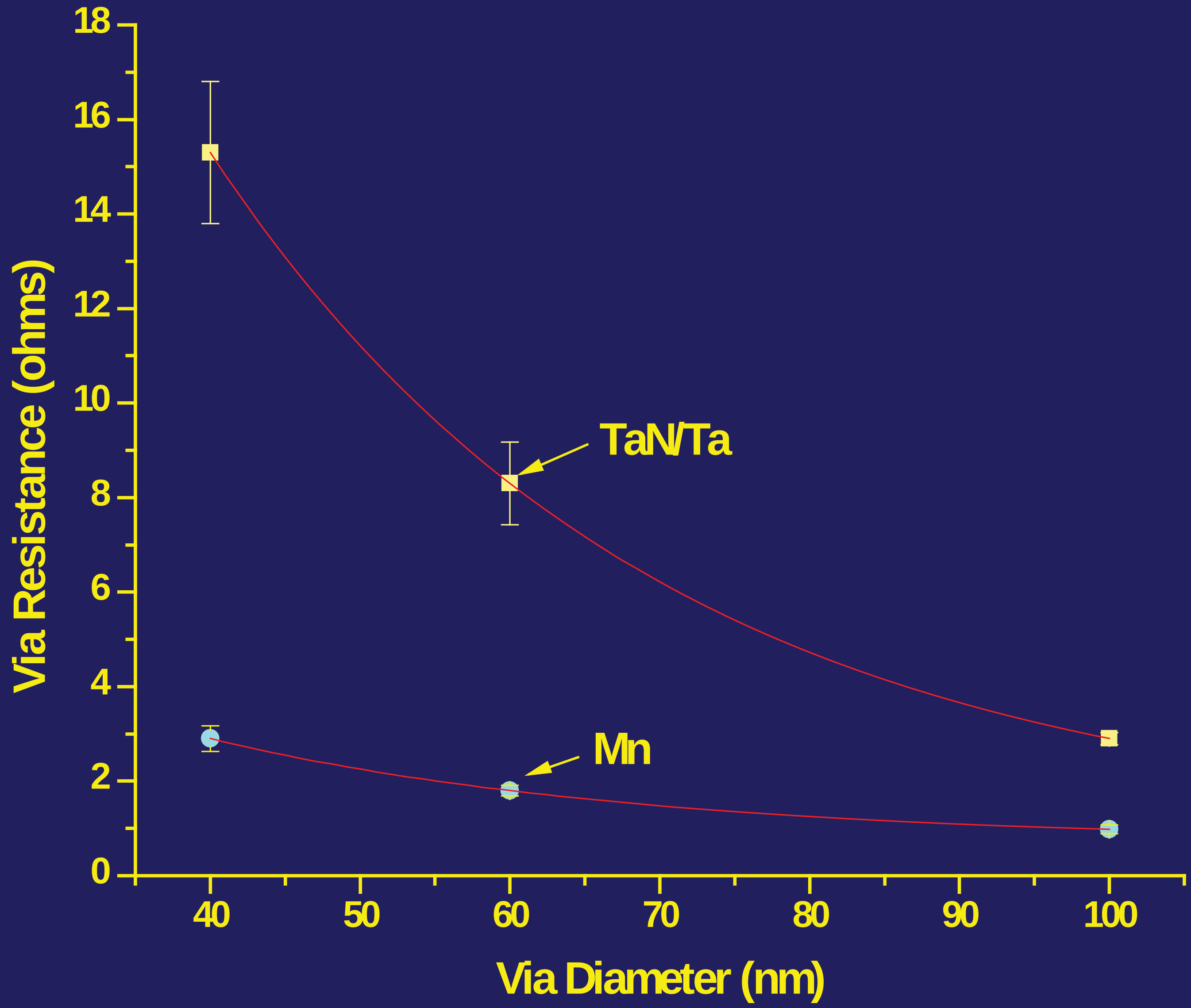
TEM analysis shows no Mn here

conventional Ta adds resistance



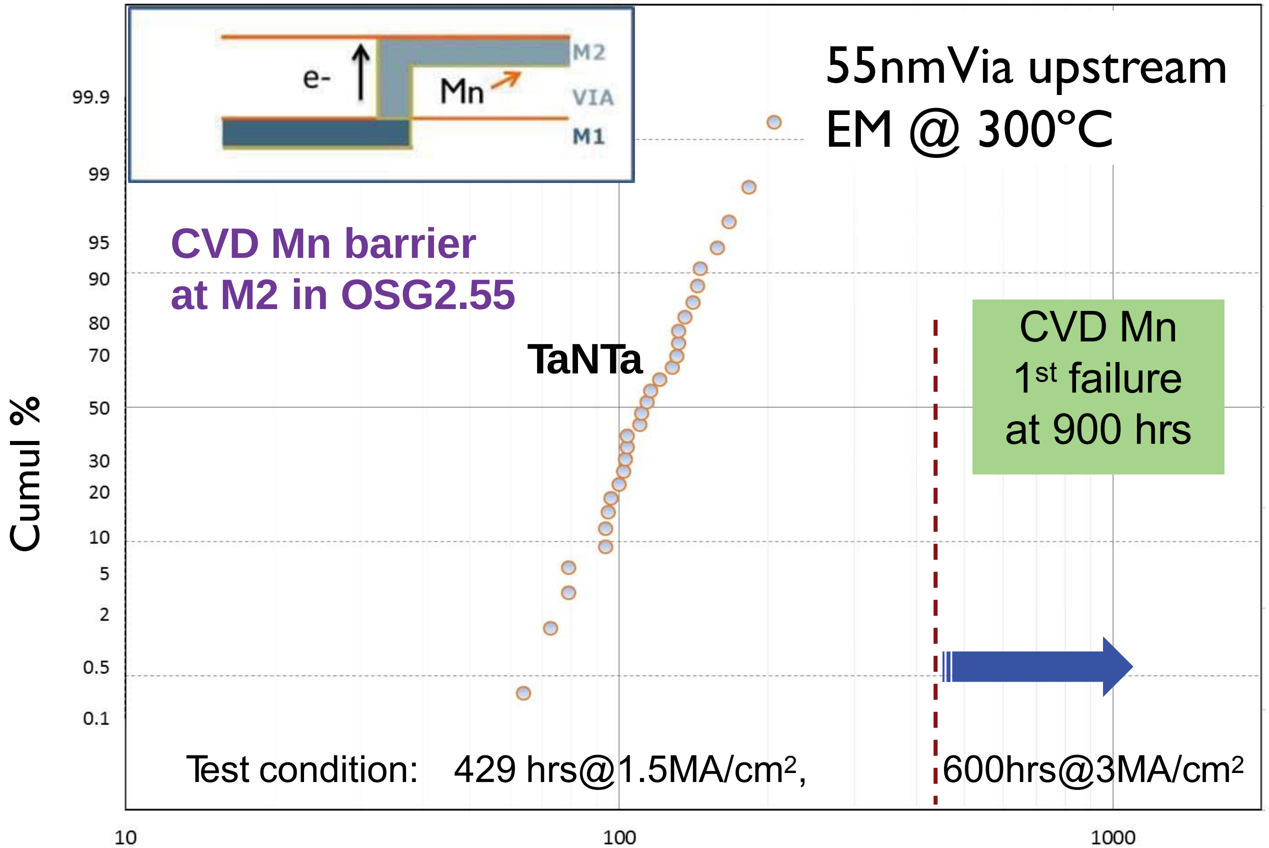
Data from AMAT and IMEC, Y. K. Siew et al., IITC 2013

Cu Via Resistance Reduction by Mn Barrier



Data from AMAT and IMEC, Y. K. Siew et al., IITC 2013

ElectroMigration (EM) failure time



- Upstream EM test shows more than
- 10x longer lifetime with CVD Mn than TaN/Ta
- because Cu-Mn bonds are stronger than Cu-Ta bonds

Types of Selective Depositions

Substrate composition

different reactivities with different materials

deactivation of reactive sites on certain materials

different diffusion rates into different materials

Substrate structure

faster growth on tops of holes

Example: sealing pores in porous dielectrics with SiO_2

faster growth on bottoms of holes

Rapid ALD of Alumina-Doped Silica from $AlMe_3$ and $(^tBuO)_3SiOH$

tris(*tert*-butoxy)silanol: $(^tBuO)_3SiOH$

$2\ AlMe_3 + 150\ (^tBuO)_3SiOH \rightarrow Al_2O_3(SiO_2)_{150}$ + volatile byproducts

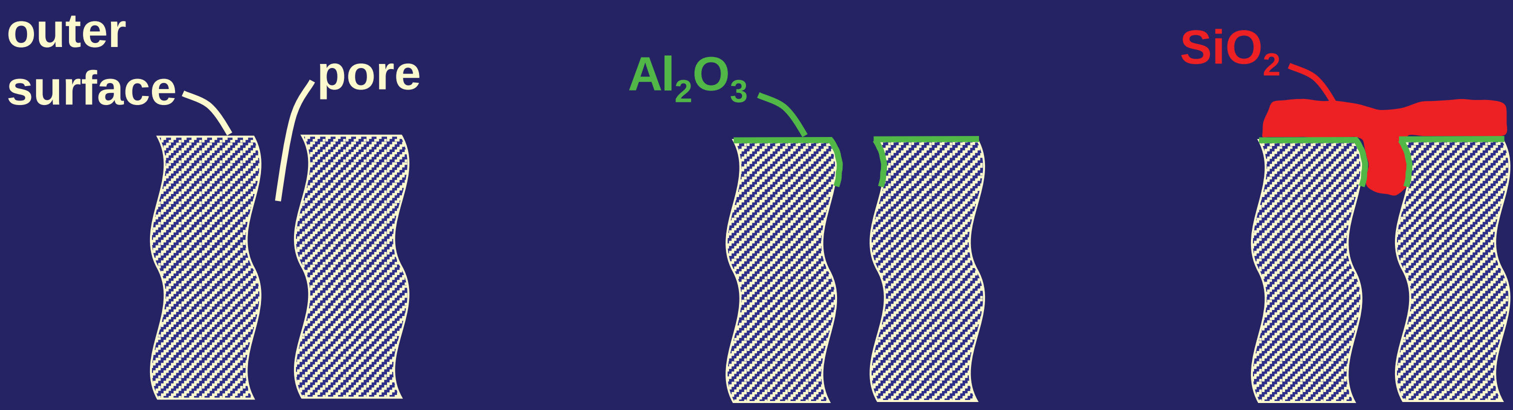
- ALD rate: up to 15 nm per cycle!
- Si to Al ratio ~70:1

- Ideal ALD behavior for substrates from 200 to 300 ºC
- Pure amorphous silica-rich aluminum silicate deposited

- Al-catalyzed polymerization and crosslinking mechanism:

D. Hausmann, J. S. Becker, S. Wang and R. G. Gordon, *Science* 298, 402 (2002)

Sealing Pores in Low-k Dielectrics Using Me_3Al (TMA) and $(^tBuO)_3SiOH$



porous low-k

with 1/3 monolayer of alumina by low-dose of TMA

with silica sealant

Limited exposure to TMA limits penetration into pores

<u>One</u> ALD cycle => ~ 6 nm of SiO_2 is enough to seal pores

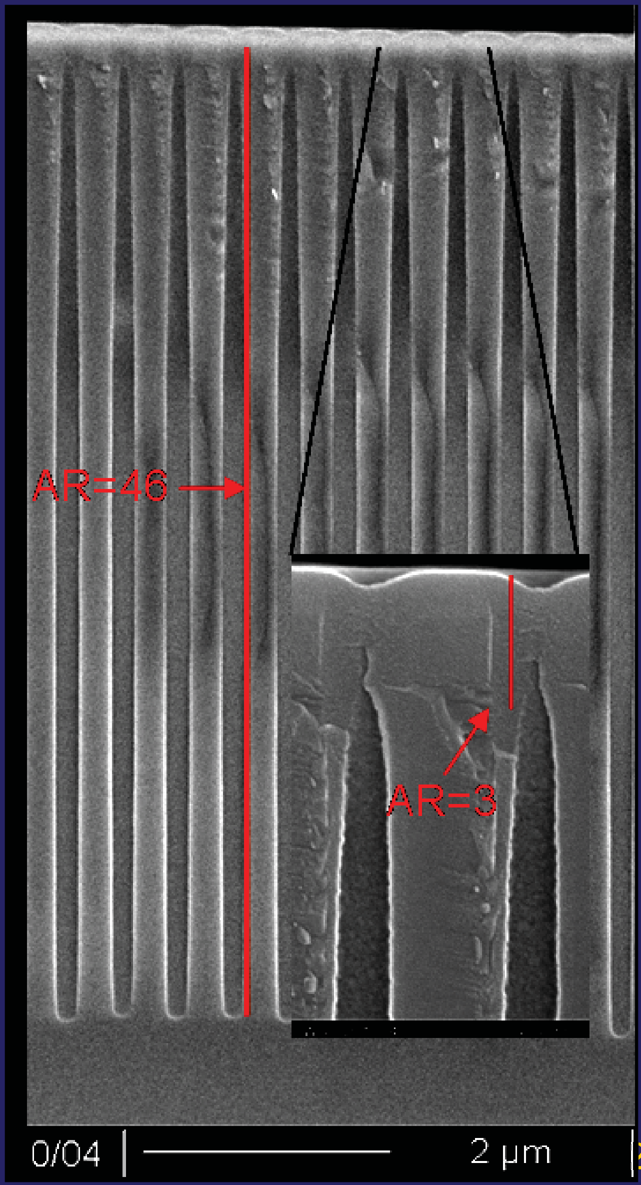
No deposition on chamber walls if 2 separate chambers used

Visualizing Sealed Pores in Test Holes

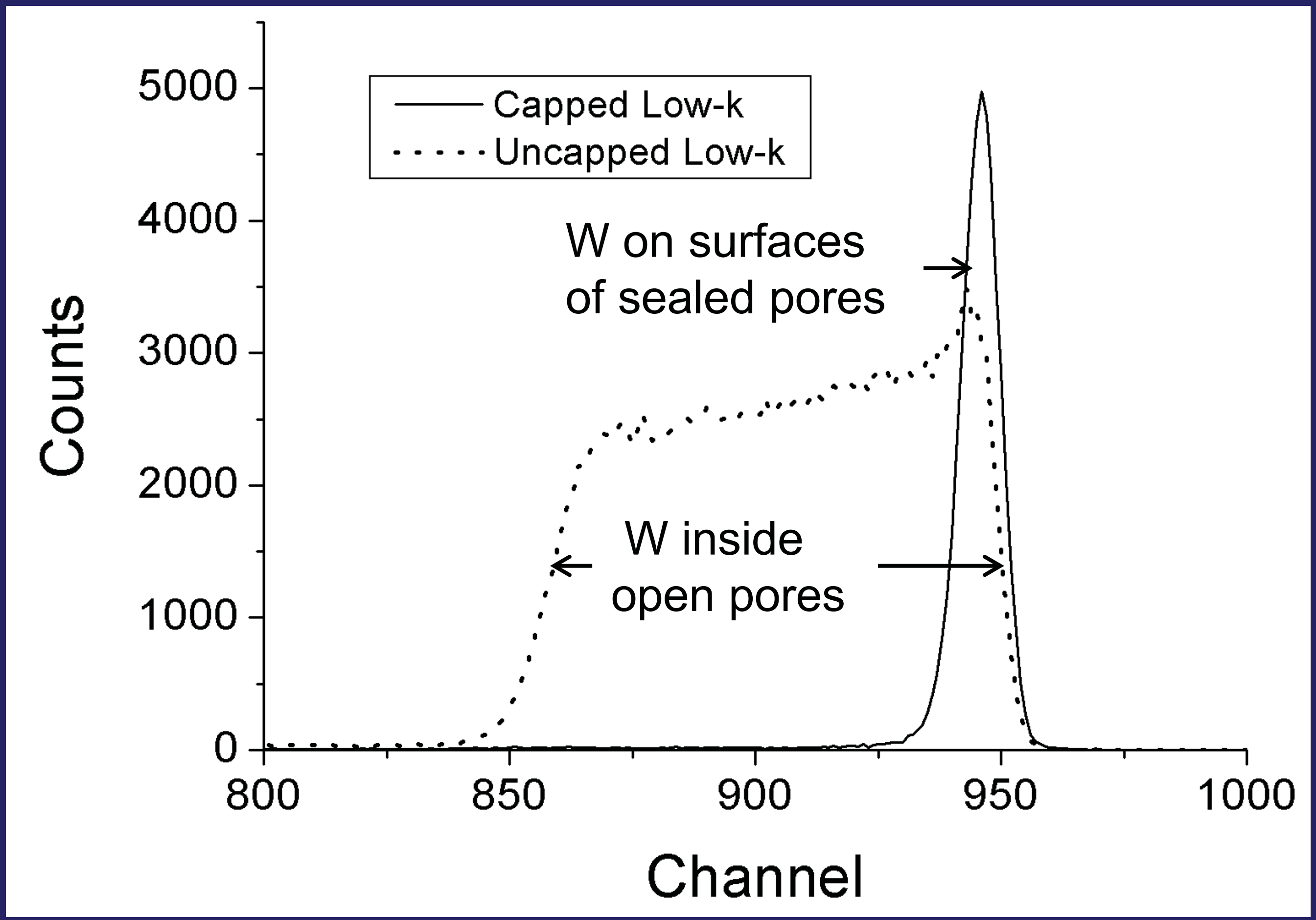
Cross section of narrow trenches sealed by ALD silica

SEM image at lower right shows a higher magnification image of the sealed tops of 2 holes

Faithful larger-scale model of the smaller pores in low-k dielectrics because no gas-gas collisions occur inside either holes.
(mean free path >> hole diameters)

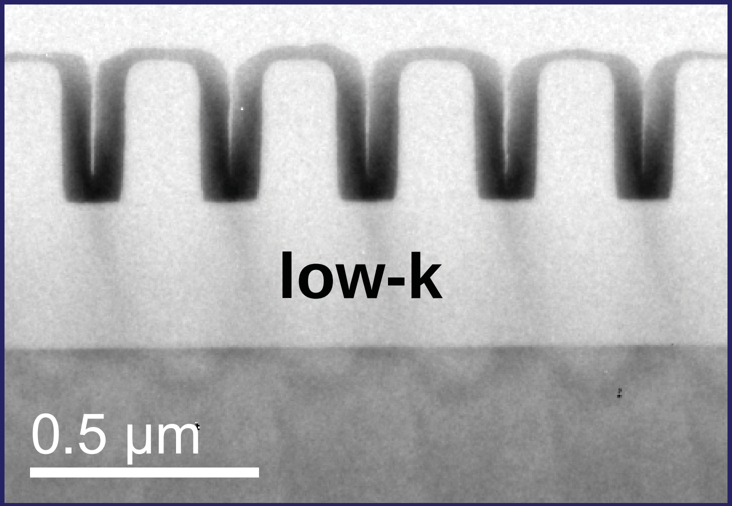


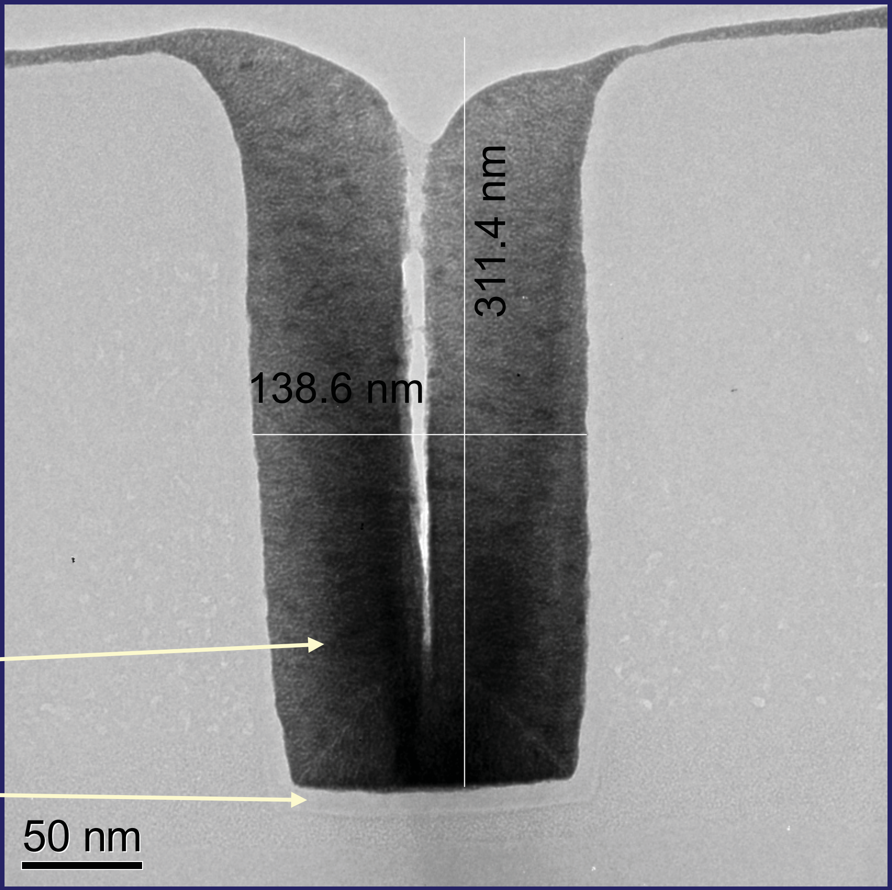
RBS Shows No Penetration of ALD WN into Sealed Pores in Low-k Dielectrics



de Rouffignac et al., *Electrochem. Solid-State Lett.*, 7, G306-G308 (2004)

TEM Shows No Penetration of ALD WN into Pores in Sealed Low-k Dielectric





ALD WN

Sealed layer

Data courtesy of SEMATECH

Selective Pore-Sealing

Want to avoid silica deposition on copper at via bottoms.

Alkylthiols react only with copper, not with low-k insulators.

Alkylthiol monolayer protects the copper from ALD silica.

5-8 nm SiO_2 seals pores, while < 1 nm SiO_2 on copper.

Types of Selective Depositions

Substrate composition

different reactivities with different materials

deactivation of reactive sites on certain materials

different diffusion rates into different materials

Substrate structure

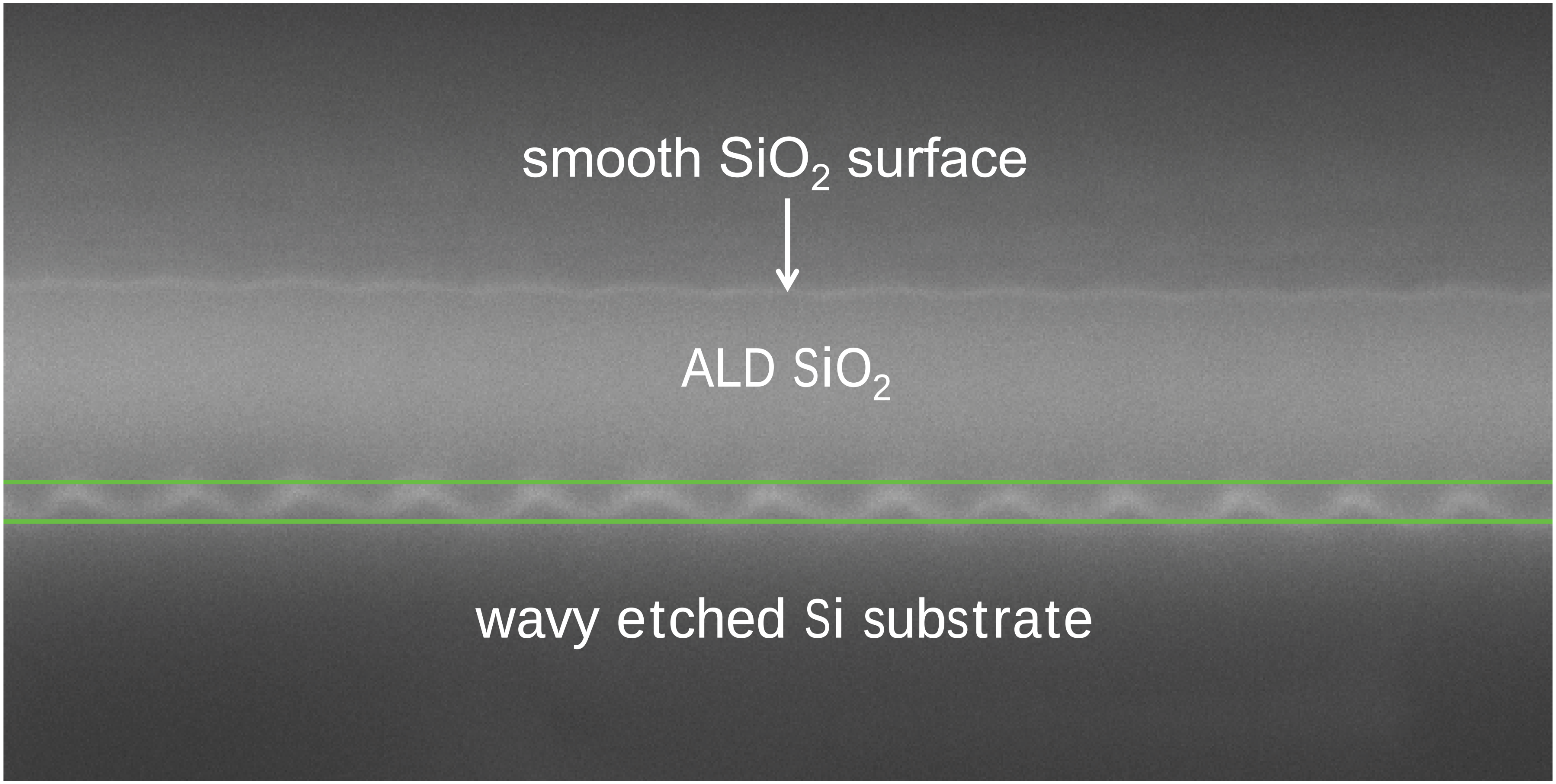
faster growth on tops of holes

faster growth on bottoms of features

Example: SiO_2 smoothening of rough surfaces

Smoothing Rough Surfaces with ALD SiO_2

Use saturating doses of TMA and tris-*tert*-pentoxysilanol



Smoothening Rough Surfaces with ALD SiO_2

1) High dose of TMA uniformly covers surface with Al catalyst

2) Dose of *tert*-pentoxysilanol grows short SiO polymers on Al

3) Polymers near peaks bend over because little crowding

4) Polymers near valleys don't have room to bend over

5) Crosslinking to SiO_2 freezes in these thickness differences

Types of Selective Depositions

Substrate composition

different reactivities with different materials

deactivation of reactive sites on certain materials

different diffusion rates into different materials

Substrate structure

faster growth on tops of holes

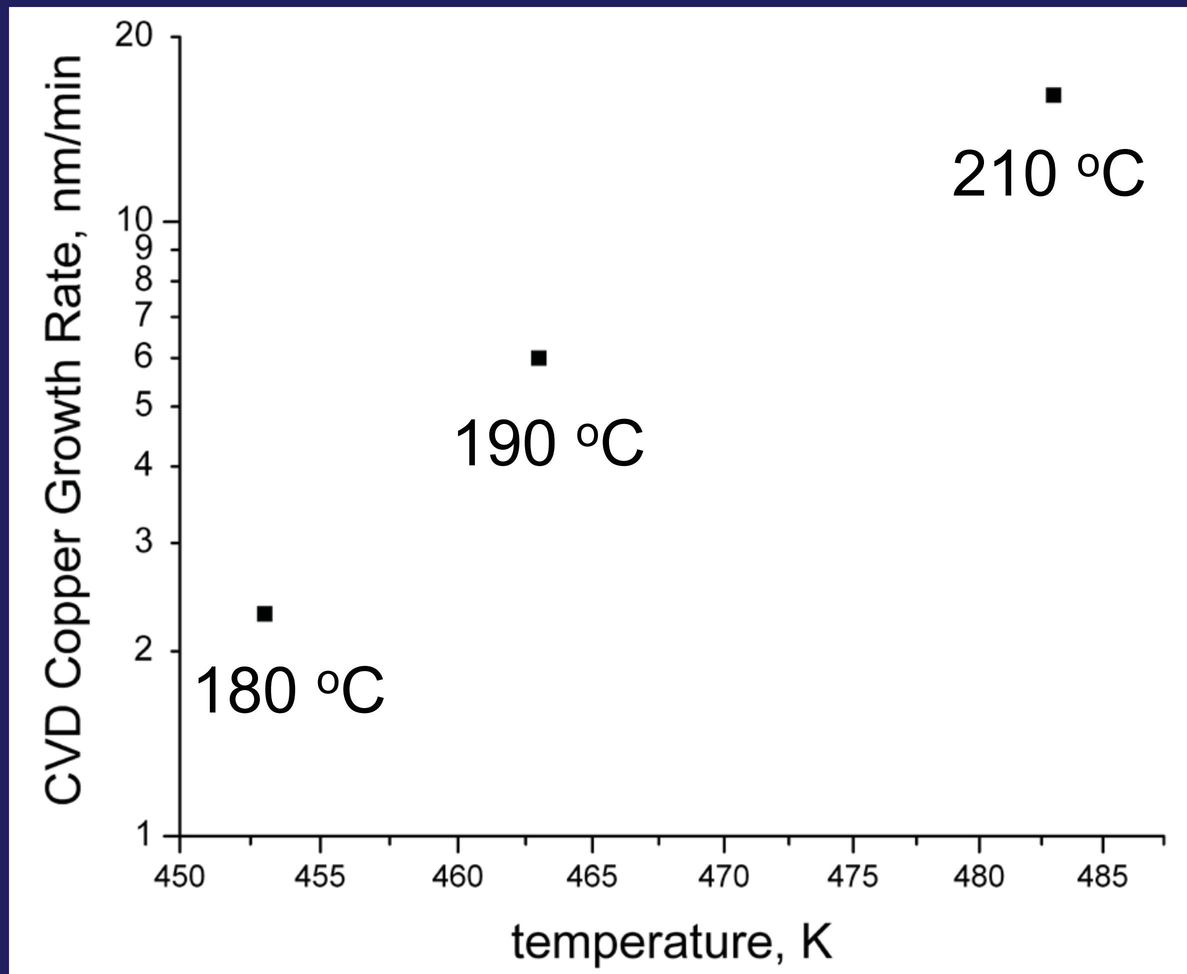
faster growth on bottoms of holes:

Example: void-free filling holes with Cu using iodine catalyst

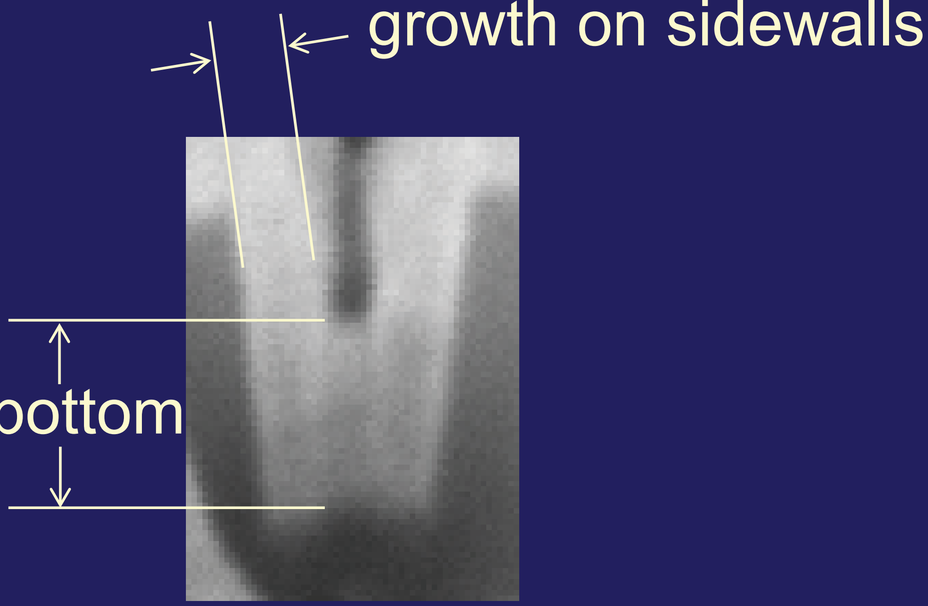
CVD Cu Growth Rate with Iodine Catalysis

Iodine "floats" on the growing surface of copper, while increasing the Cu growth rate by 10 times.

10 nm trench or via filled in < ½ minute



Bottom-Up Filling by CVD Copper

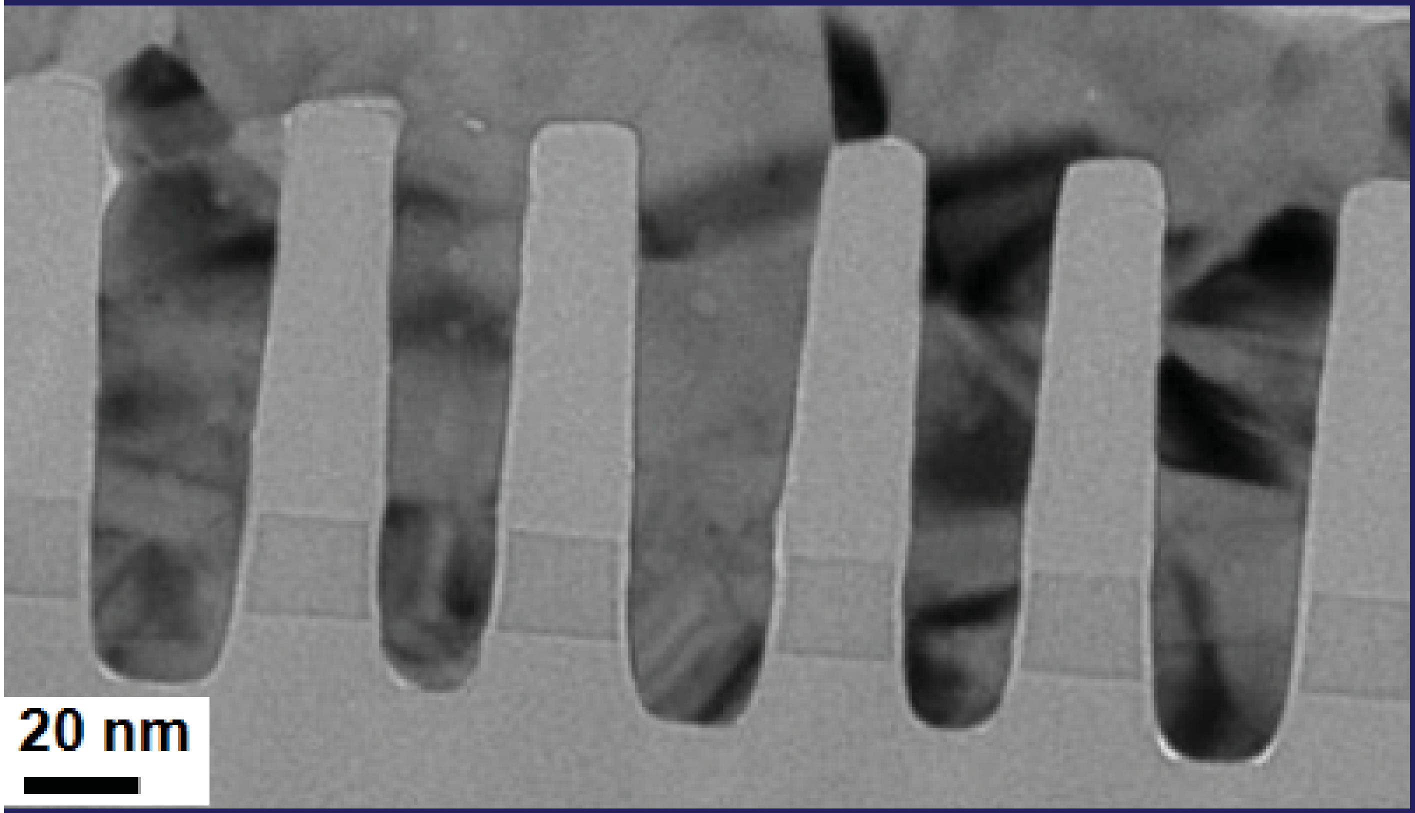


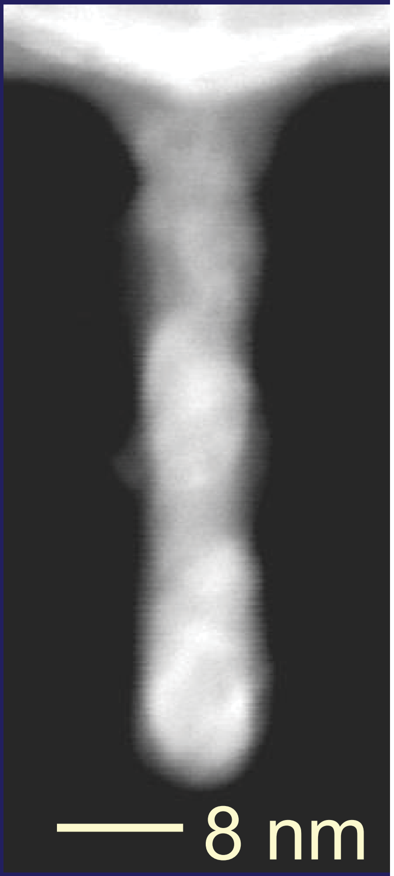
Crowding of I catalyst => faster growth from bottom than from sides

=> void-free filling of narrow trenches

Y. Au, Y. Lin and R. G. Gordon, Filling Narrow Trenches by Iodine-Catalyzed CVD of Copper and Manganese on Manganese Nitride Barrier/Adhesion Layers, *J. Electrochem. Soc.* **158,** D248-D253 (2011)

Bottom-Up Fill by Iodine-Catalyzed CVD Cu-Mn Alloy





crystallites cross trenches, no center seam

Can be scaled to the end of the roadmap

Types of Selective Depositions

Substrate composition

- **different reactivities with different materials**
  - **SiO_2 on TiO_2 vs organic dye in solar cells => increased efficiency**
- **deactivation of reactive sites on certain materials**
  - **Mn not on SiO_2 but into Cu => increased stability**
- **different diffusion rates into different materials**
  - **Mn on SiO_2 but into Cu => lower via resistance**

Substrate structure

- **faster growth on tops of holes**
  - **SiO_2 only on tops of holes => pore sealing**
- **faster growth on bottoms of holes**
  - **SiO_2 faster on bottoms => smoothing**
  - **Cu faster on bottoms => void-free fill**

Acknowledgements

Precursors supplied by Dow Chemical, Sigma-Aldrich and Strem Chemical

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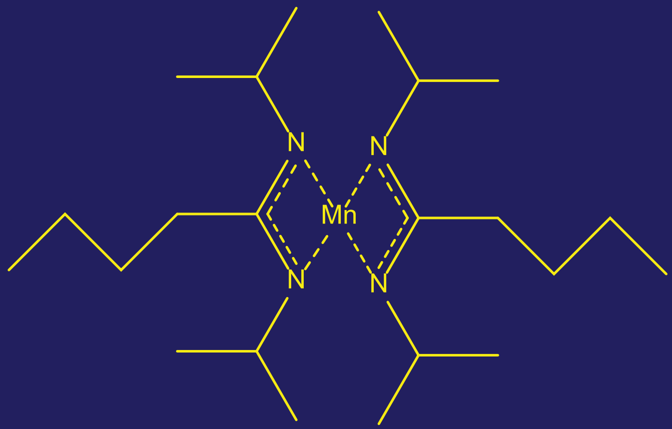
Facilities at Harvard's Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN), previously supported by the U. S. National Science Foundation

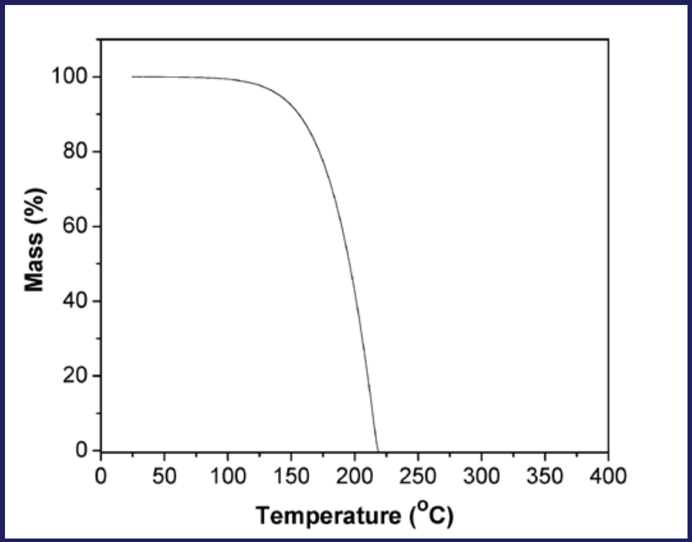
Extra Slides

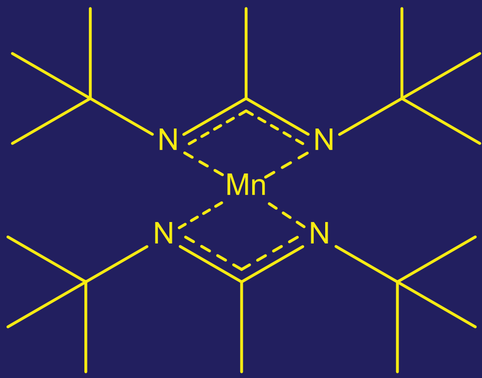
Manganese Precursors for MnN_x, $MnSi_xO_y$ and CuMn



manganese(II)
bis(*N,N'*-diisopropylpentamidinate)

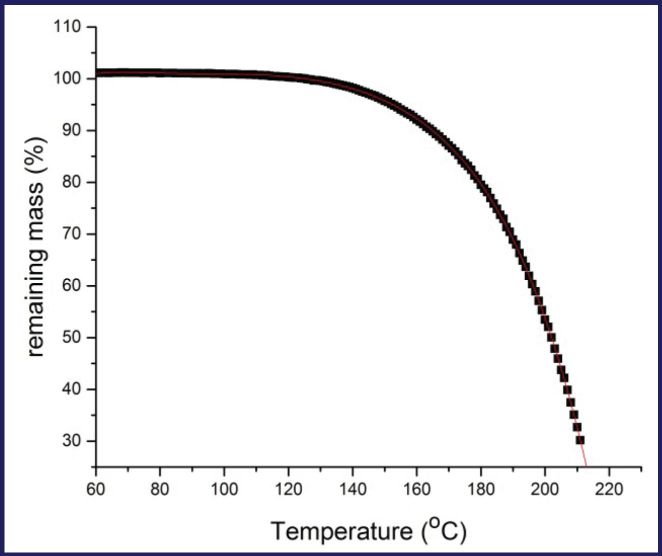
melting point: 60 °C
boiling point: 90 °C / 50 mtorr
no decomposition





manganese(II)
bis(*N,N'*-di-*tert*-butylacetamidinate)

melting point: 107 °C
boiling point: 100 °C/ 70 mtorr
no decompoistion



Manganese-Stabilized Copper Interconnects

CVD of MnN_x uniformly inside narrow lines and vias

$MnN_x + SiO_2 \Rightarrow MnSi_yO_zN_w$, blocking diffusion of Cu, H_2O and O_2 and adhering strongly to SiO_2

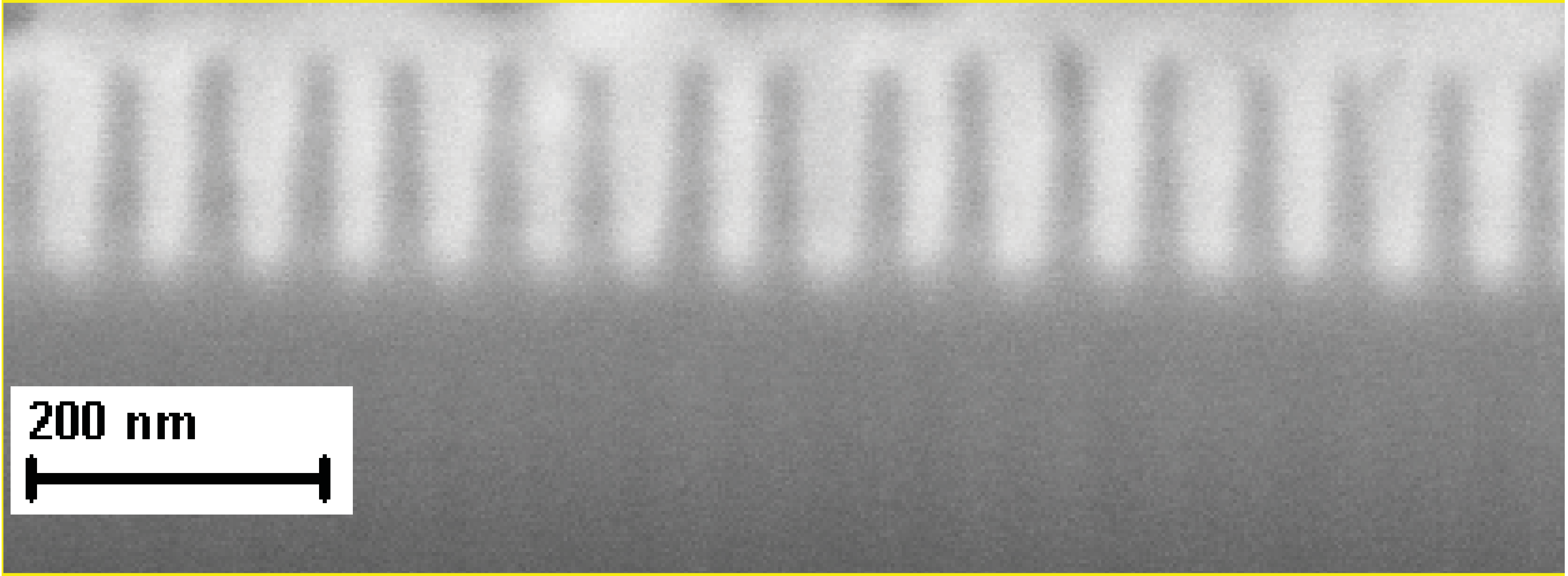
MnN_x chemisorbs iodine and then releases it to catalyze void-free, super-conformal CVD of copper-manganese alloy

CVD Cu-Mn adheres strongly to MnN_x

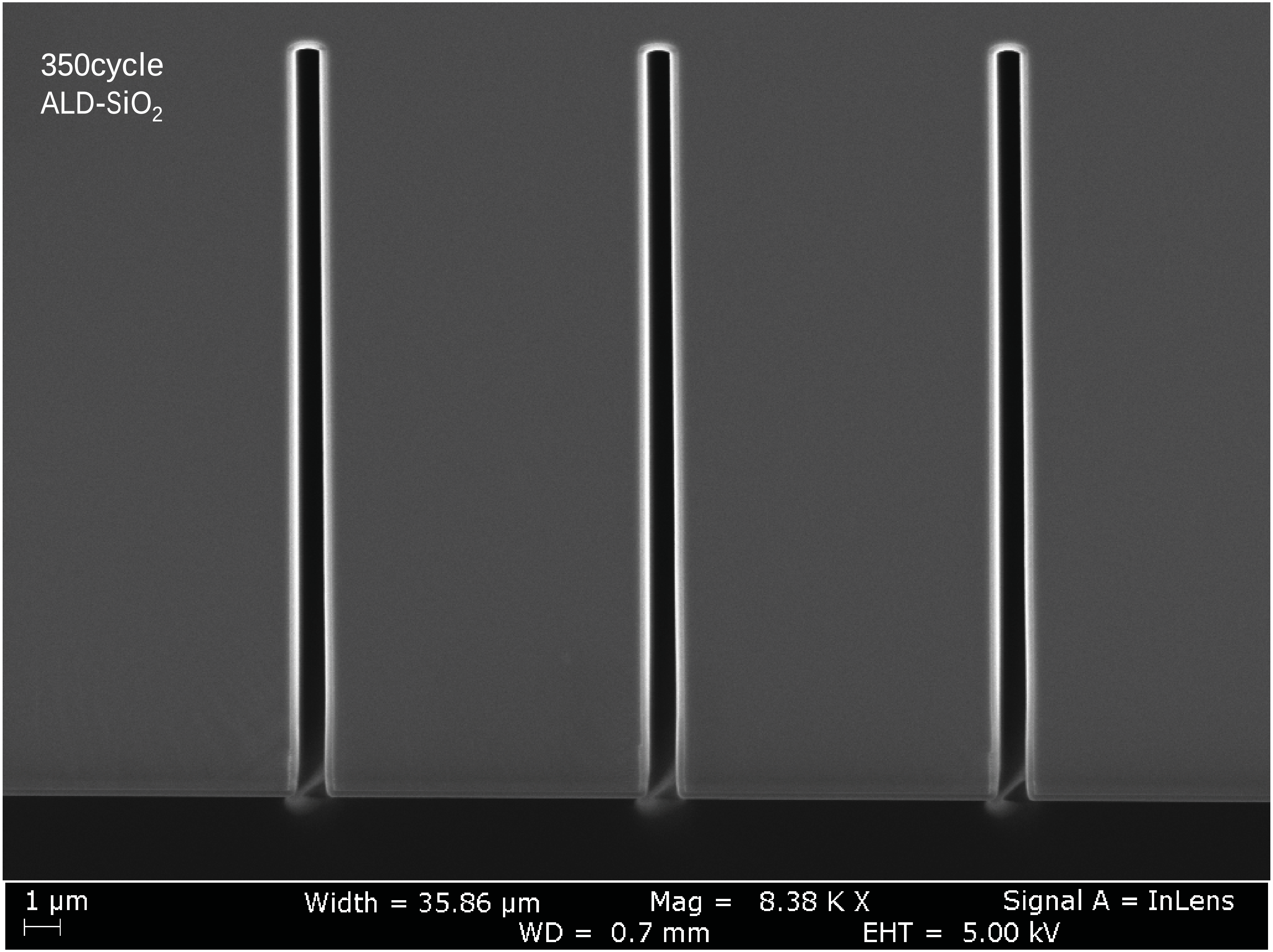
MnN_x at bottoms of vias dissolves into Cu during annealing, allowing direct, low-resistance contact between levels of metallization

Bottom-Up Fill by Iodine-Catalyzed CVD Cu-Mn Alloy

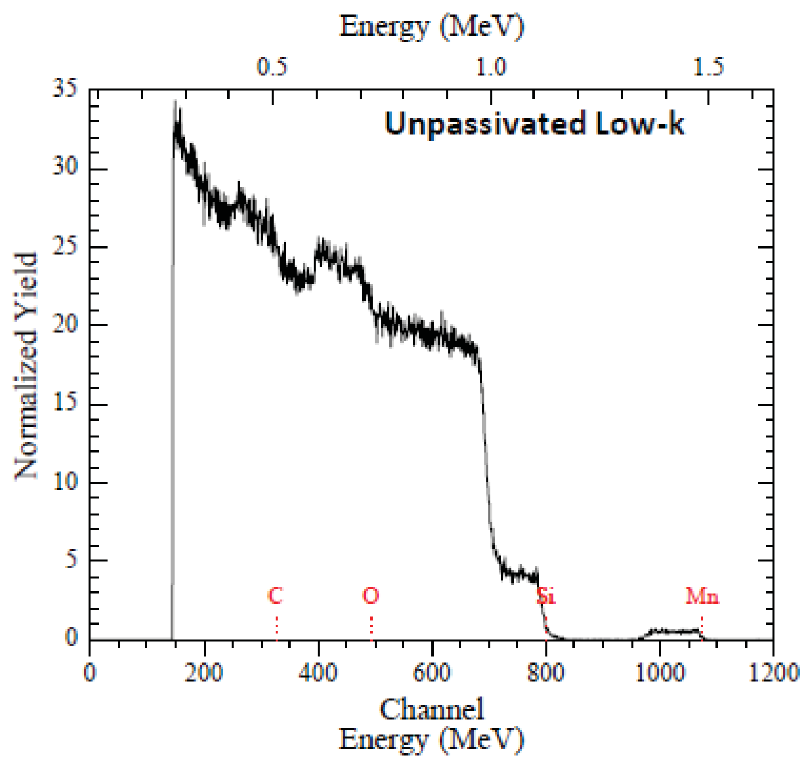
SEM of Cu-Mn in trenches with width ~ 27 nm



After anneal, Mn diffuses to interfaces between Cu and insulator, provides strong adhesion and diffusion barrier to Cu, H_2O and O_2.

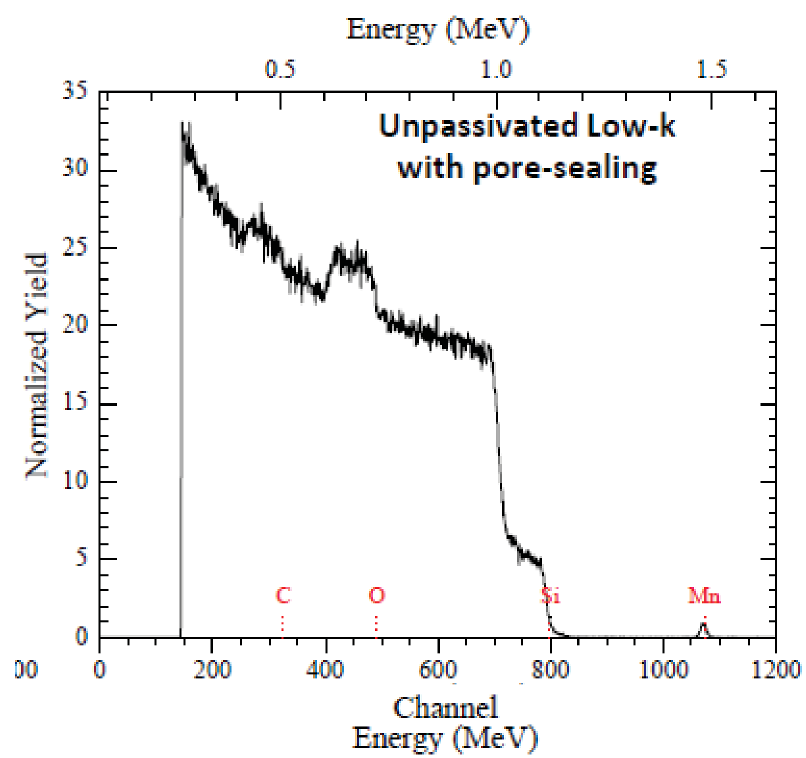

350cycle
ALD-SiO_2
1 µm
Width = 35.86 µm
Mag = 8.38 K X
Signal A = InLens
WD = 0.7 mm
EHT = 5.00 kV

CVD Mn on Unpassivated SiCOH (2.2)



The width in energy of the Mn peak is the same as the widths of Si, O and C, demonstrating that Mn was deposited throughout the thickness of the insulator.

CVD Mn on Unpassivated & Pore-Sealed SiCOH (2.2)



The width in energy of the Mn peak is much smaller than the widths of Si, O and C, demonstrating that Mn was deposited only on the surface of the insulator.